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(54) Absorbent formulation for enhanced removal of acid gases from gas mixtures and processes using same.

(57) Acid gas absorption of H<sub>2</sub>S by select aqueous alkaline absorbents, is enhanced by adding low pK<sub>a</sub> acid or acid-forming material providing acid sufficient to protonate up to 22% of the absorbent, thereby altering the absorbent-acid gas vapor-liquid equilibrium.

*monoamines + strong acid up to 22% protonation  
to  $\downarrow$   $\text{ppm}_{\text{out}}$  <sup>H<sub>2</sub>S</sup>, to stream, ↑ selectivity CO<sub>2</sub>*

CROSS REFERENCE TO RELATED APPLICATION

5 This application is a continuation-in-part  
of U.S. Patent Application Serial No. 509,455, filed  
June 30, 1983, now abandoned.

BACKGROUND OF THE INVENTION

Field of the Invention

0 This invention relates to the removal of  
acid gases from gaseous mixtures and to compositions  
useful in the manufacture of aqueous alkaline  
absorbents. The compositions are expressly  
characterized by their efficiency in removing acid  
5 gases, such as  $H_2S$ , from gaseous mixtures. Such  
gaseous mixtures include natural gases, refinery  
gases, Claus gases, coke oven off gases, coal  
gasification gases, landfill gases, any synthetic  
gas product and the like. The composition is  
0 particularly effective in removing acid gas from low  
pressure gas streams containing  $H_2S$ .

Description of the Prior Art

5 Much research and effort has been expended  
for the purpose of improving the treatment of gas  
streams to remove acid components.

Aqueous alkanolamine solutions have been  
used for over 50 years to remove acid gas components  
from gas streams. Hydrogen sulfide ( $H_2S$ ) is very  
toxic and must be removed before high pressure  
natural gas streams can enter a pipeline system.  
1  $H_2S$  is also removed from lower pressure refinery

gas streams and from atmospheric pressure Claus tail  
gas treating units. Two deficiencies exist in the  
state of the art amine-based technology for these  
applications. First,  $H_2S$  absorption into the  
5 amine solutions becomes more difficult at lower gas  
pressures simply due to the lower  $H_2S$  partial  
pressure driving force. At the high pressures of  
most natural gas streams,  $H_2S$  generally can be  
easily removed down to the 4 ppm pipeline  
10 specification. This specification often cannot be  
met at the lower pressure of refinery gas streams.  
The 10 ppm  $H_2S$  specification for the very low  
pressure Claus tail gas streams is essentially  
impossible to achieve by amine treating and is dealt  
15 with by costly post incineration which converts the  
 $H_2S$  not removed by absorption to  $SO_2$  which has a  
higher specification. Unfortunately,  $SO_2$  is  
suspected as being responsible for forming "acid  
rain" and it is highly desirable to avoid its  
20 introduction into the atmosphere.

A second disadvantage is that the primary  
and secondary amines conventionally used in  
absorbent solutions also coabsorb  $CO_2$  which is  
often present and may not need to be completely or  
25 even partially removed. Removing  $CO_2$  adds  
directly to equipment sizes and processing costs  
which are significant at current energy prices.  
Furthermore, avoiding  $CO_2$  removal is vital to  
Claus tail gas processing when the absorbed  $H_2S$  is  
30 recycled to the Claus unit. Recycling  $CO_2$ , an  
inert gas, significantly dilutes the  $H_2S$  stream,  
often to the point that a conventional Claus reactor

cannot function. Diisopropanolamine (DIPA) and methyldiethanolamine (MDEA) exhibit kinetic selectivity for  $H_2S$  over  $CO_2$  due to a relatively slow hydration step that  $CO_2$  must undergo to form carbonic acid before reacting with these amines.  $H_2S$  does not have to go through this step and can react directly with these amines resulting in a much faster rate of absorption. These amines exhibit "kinetic" selectivity and can be used in processes which have been designated to exploit the much faster absorption rate of  $H_2S$  compared to  $CO_2$  to achieve selective  $H_2S$  removal. Nonetheless, some  $CO_2$  is still removed in such methods of use and further improvement in the kinetic selectivity properties of such solvents is desirable.

U.S. Patent No. 2,718,454 describes a process for using potash and similar alkali metal salts in conjunction with amines such as monoethanolamine, diethanolamine and triethanolamine to remove acid gases from a gas mixture. The combination of alkali metal compounds in conjunction with the designated amine allegedly yields the higher capacity for acid gases than systems using the amines alone.

U.S. Patent No. 3,144, 301 discloses the use of potassium carbonate in conjunction with diethanolamine and monoethanolamine to remove  $CO_2$  from gas mixtures.

U.S. Patent Nos. 3,637,345, 3,763,434 and 3,848,057 disclose processes for removing acid gases by using aqueous carbonate scrubbing solutions activated by an amine. U.S. Patent No. 3,848,057

describes in addition the addition of a weakly  
acidic  $\text{CO}_2$  hydration catalyst such as boric acid,  
sulfurous acid or formaldehyde but specifies amounts  
of such acidic materials far in excess of those  
5 amounts that are useful in achieving the advantages  
of the present invention. Furthermore, U. S. Patent  
No. 3,848,057 is concerned with the kinetics of  
 $\text{CO}_2$  removal using boric acid and other weak acidic  
 $\text{CO}_2$  hydration catalysts to speed up the absorption  
10 of  $\text{CO}_2$  and is not concerned with altering the  
vapor-liquid equilibria of gases containing  $\text{H}_2\text{S}$   
and absorbents in contact therewith. Boric acid  
which is the weak acid preferred by this patent is  
inoperative in the present invention. The amounts  
15 of the weak acidic  $\text{CO}_2$  hydration catalyst  
disclosed as most advantageous by U. S. Patent No.  
3,848,057 are not only inoperative in the present  
invention but are counter-productive in producing an  
off gas that is higher in  $\text{H}_2\text{S}$  content than the  
20  $\text{H}_2\text{S}$  content of an off gas where no acid is used.

U.S. Patent No. 3,856,921 discloses a  
process for removing acid gas by use of a basic salt  
of an alkali or alkaline earth metal and an amine  
activator.

25 British Patent No. 1,063,517 also discloses  
the use of potassium carbonate and potassium borate  
in conjunction with particular amines to avoid  
corrosion problems and accelerate the absorption and  
subsequent deabsorption of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ .

30 U.S. Patent Nos. 3,856,926, 3,685,960 and  
3,896,212 teach the improvement of  $\text{CO}_2$  absorption  
rates into alkali metal salt solutions by adding

small amounts of water soluble, substituted amines.  
The improvements as claimed in these patents as well  
as all those mentioned hereinabove are purely  
kinetic and none of these patents discuss any  
5 improvements due to alterations in the equilibrium  
curves. It is known that CO<sub>2</sub> absorption in  
substantially all regenerable basic mediums is mass  
transfer limited. Therefore, equilibrium changes at  
low CO<sub>2</sub> concentrations could not be perceivable  
10 under dynamic conditions and certainly could not be  
useful.

U.S. Patent Nos. 3,622,267 and 4,336,233  
both discuss improved CO<sub>2</sub> absorption rates  
obtained by adding small amounts of certain  
15 secondary amines to solutions of tertiary amines  
which, when used alone, exhibit extremely slow CO<sub>2</sub>  
absorption rates. The improved CO<sub>2</sub> absorption  
rates are however kinetic and not an equilibrium  
phenomenon.

20 U.S. Patent Nos. 4,112,050 and 4,112,051  
disclose improvements due to alterations in  
equilibrium curves for CO<sub>2</sub> absorption obtained at  
high CO<sub>2</sub> concentration levels. Increased  
absorption capacity results when sterically hindered  
25 amines are added to potassium carbonate solutions.  
Equilibrium effects resulting in lower CO<sub>2</sub> levels  
in the absorber off gas are not expressly disclosed  
or obvious in the disclosure of these patents. U.S.  
Patent No. 4,112,051 discusses the application of  
30 the hindered amine concept to non-aqueous solutions.

U.S. Patent Nos. 2,937,071, 3,037,844,  
3,086,838 and 3,395,978 each disclose the use of

alkali metal arsenite compounds as additives to potassium carbonate absorbing solutions or alone in absorbing solutions to yield greater  $\text{CO}_2$  absorption rates through kinetic means rather than equilibrium means.

U. S. Patent No. 3,139,324 (Housset) discloses a process for removing  $\text{CO}_2$  and  $\text{H}_2\text{S}$  from gaseous mixtures using a mixture of ethanolamine and a weak acid. The only disclosed relative amounts of ethanolamine to acid are 2:1 molar. Such a process is disclosed as removing the disturbing action of  $\text{CO}_2$  on the dissolution in water of sulfuretted hydrogen without hindering the dissolution of the actual carbon dioxide.

U. S. Patent No. 4,080,423 (Smith et al.) discloses a system for improving the rate of acid gas adsorption by using an alkaline absorbent in combination with a weak acid having a  $\text{pK}$  greater than 7.

U. S. Patent No. 2,722,500 (Rippie et al.) pertains to a process for removing  $\text{H}_2\text{S}$  and  $\text{CO}_2$  from liquid and gaseous petroleum products such as natural gas, by using an alkanolamine in conjunction with a dual ionizing acid. The disclosed process is directed towards removing volatile acidic substances from liquid hydrocarbons utilizing primarily triethanolamine phosphate.

U. S. Patent No. 4,153,674 (Verloop et al.) concerns a process for recovering sulfur from sulfur-compound containing gases by reducing all sulfur constituents of the gas mixture in the presence of recycled off-gas followed by absorption using a liquid and regeneratable hydrogen-sulfide

absorbent such as alkanolamines. It is disclosed that a strong acidic compound may be added to the alkanolamine absorbent to reduce the amount of stripping steam required and to lower the amount of unabsorbed hydrogen sulfide. Preferably, enough acidic compound is added to acidify 0.1 to 15 mole % of the alkanolamine.

None of the above-mentioned patents however disclose, teach or suggest the use of a relatively small amount of an acid having a  $pK_a$  of 6 or less or acid-forming material capable of forming an acid having a  $pK_a$  of 6 or less in aqueous medium wherein said acid or acid-forming material are added to an alkaline scrubbing liquid containing a select alkaline absorbent in an amount sufficient to protonate more than 0% and up to 22% of said alkaline absorbent to provide enhanced acid gas removal.

#### SUMMARY OF THE INVENTION

This invention is based on the discovery that vapor-liquid equilibria of aqueous alkaline absorbent solutions are favorably altered to yield more efficient absorption and stripping of acid gases containing  $H_2S$  from gaseous mixtures containing same by the addition of very small amounts of acid or acid-forming material to a specific class of absorbents. It has been found that this effect is pronounced at low acid gas concentrations in the gaseous mixture which results in even lower concentrations in the treated gaseous mixture. This can be of a particular benefit in treating Claus tail gas where  $H_2S$  needs to be



removed down to 10 ppm to satisfy environmental regulations. Under current absorption technology heretofore available in the prior art, it has been possible to achieve  $H_2S$  removal in Claus tail gas only down to 100 to 250 ppm. In order to bring the  $H_2S$  content down to acceptable levels, it is current practice to incinerate the residual  $H_2S$  to  $SO_2$  which has been accorded a higher allowable limit under current EPA regulations. Aside from the fact that such incineration is quite costly, it appears to be the consensus that the release of  $SO_2$  into the atmosphere is the chief responsibility for the production of "acid rain."

The present invention provides a striking improvement in the efficiency of a cyclic absorption/regeneration process when small amounts of a relatively strong acid are added to particular aqueous alkaline absorbents. Surprisingly the relatively strong acid shifts the vapor/liquid equilibrium curve at low acid gas ( $H_2S$ ) concentrations to afford a greater degree of acid gas ( $H_2S$ ) removal.

The invention provides compositions for mixing with water to provide an aqueous alkaline liquid for scrubbing acid gases. The invention also provides aqueous alkaline solutions for scrubbing acid gases and it also provides procedures and methods for removing  $H_2S$  as a constituent from gases by washing the gases with a select aqueous alkaline scrubbing material containing relatively small amounts of relatively strong acids and subsequently regenerating the scrubbing liquid.

Tripotassium phosphate ( $K_3PO_4$ ) was promoted in the 1950's as a selective solvent for absorbing  $H_2S$  from gas streams containing  $H_2S$ ,  $CO_2$ , and inerts. In pursuit of a goal to further improve the selective properties of an MDEA-based formulation, a test program was conducted to determine if a combination of MDEA and  $K_3PO_4$  could provide a synergistic improvement. Initial absorber results showed no effect on  $CO_2$ , but did show enhanced  $H_2S$  removal. Improved selectivity was implied because fewer absorber trays would be needed for  $H_2S$  removal and by using less trays  $CO_2$  absorption could be reduced. However, it was found that the stronger basicity of  $K_3PO_4$  hindered regeneration which is essential in commercial practice. In fact, it was discovered that  $K_3PO_4$  actually decreased  $H_2S$  removal under cyclic use conditions. This result was unexpected and led to further investigation of the absorption/regeneration nature of MDEA at low  $H_2S$  concentrations. It was theorized pursuant to this invention that perhaps a base weaker than MDEA or even an acid might produce the opposite effect when added to MDEA and thereby enhance  $H_2S$  removal. Tests with  $K_2HPO_4$  which has a basicity close to that of MDEA, produced results similar to that of MDEA only. This is expected according to the theory of the present invention. Tests with small amounts of  $H_3PO_4$  in MDEA have shown an increase in the total  $H_2S$  removed under cyclic use conditions. The results also indicate that there is an optimum  $H_3PO_4$  concentration of about 1.4% in 50:50

MDEA:water scrubbing solution which yields the maximum improvement. Other acids show similar results. It is theorized that the presence of a small amount of acid favorably alters the  $H_2S$ -MDEA vapor-liquid equilibria curve and improves overall  $H_2S$  removal particularly at low  $H_2S$  concentrations found at the lean (top) end of the absorber and at the lean (bottom) end of the stripper.

10 By studying the absorption of  $H_2S$  and  $CO_2$  in a laboratory absorber and focussing on the performance at the top of the absorber where  $H_2S$  concentrations are low, it was discovered that the addition of small amounts of soluble compounds with  
15 a pH different from 50% aqueous MDEA changed the degree of  $H_2S$  removal or the concentrations of  $H_2S$  in the absorber off gas. To simulate a cyclic process, MDEA solutions were prepared containing amounts of  $H_2S$  and  $CO_2$  representative of the  
20 rich solution following an absorption. These solutions were stripped under constant and identical conditions to produce a lean solution for the absorption experiments. It was recognized that additives that affect absorption are also likely to  
25 affect desorption which necessitates that the entire cyclic process be simulated. By this method, it has been found that compounds having a higher pH than that of MDEA hinder  $H_2S$  removal and yield higher  $H_2S$  levels in the absorber off gas. Compounds of  
30 lower pH enhance  $H_2S$  removal. An explanation is offered that the compounds alter the shape of the MDEA- $H_2S$  vapor-liquid equilibrium curve which in

turn affects the efficiency and degree of  $H_2S$  removal in a cyclic system employing an absorber and a stripper, each having a finite number of trays. Adding a small amount of an acidic compound pursuant to this invention produces the favorable effect of enhanced  $H_2S$  removal. Acids, such as phosphoric acid, whose anions exhibit low corrosivity in basic medium are preferred. It was also learned that maximum  $H_2S$  removal occurs when the phosphoric acid concentration is in the range of 0.5-2.5% based on the total weight of a 50:50 MDEA:water absorbing solution containing same. At higher concentrations the MDEA becomes significantly neutralized by the acid and begins to lose the necessary basicity to remove  $H_2S$ .

The improvement of the MDEA-acid aqueous mixture in enhancing the removal of  $H_2S$  can be exploited in three ways:

- 1) Maintain process conditions constant and produce an absorber product gas lower in  $H_2S$  content.
- 2) Employ less absorber trays such that  $H_2S$  removal is the same as if no acid were present. This will result in less  $CO_2$  absorption, thus improving the selectivity. A further benefit will be a reduced reboiler energy demand because of the reduced  $CO_2$  load.
- 3) If employing less absorber trays is not possible because multiple lean solution feed points are not available, energy savings can be realized by reducing the reboiler rate until the  $H_2S$  level in the absorber off gas increases to the

level without the acid present. The effective concentration range is 0-4.5%  $H_3PO_4$  and the optimum is .5-2.5% based on the total weight of a 50:50 MDEA:water absorbing solution containing same.

5                    DETAILED DESCRIPTION OF THE INVENTION

                  In accordance with this invention, the novel compositions for mixing with water to provide aqueous, alkaline liquids for scrubbing acid gases containing  $H_2S$  are prepared by simply mixing an  
10                   acid having a  $pK_a$  of 6 or less or an acid-forming material capable of forming in an aqueous medium an acid having a  $pK_a$  of 6 or less with a select alkaline material in an amount sufficient to protonate more than 0% but not more than 22% of said  
15                   alkaline material. Preferably an acid having a  $pK_a$  of 5 or less and most preferably 4 or less are used and amounts sufficient to provide 0.1 to 22% and most preferably 2 to 13% protonation of the alkaline material are employed.

20                   The novel aqueous alkaline scrubbing solutions are prepared by simply mixing the above-mentioned composition with water in an amount adequate to provide 5 to about 70 wt. %, preferably 20 to 60 wt. %, of the alkaline material based on  
25                   the total weight of the scrubbing liquid or solution. Alternatively, the novel scrubbing solution can be prepared by dissolving in water a sufficient amount of the alkaline material to provide a 5 to 70 wt. %, preferably 20 to 60 wt. %, aqueous solution of said alkaline material in said  
30                   solution and mixing a sufficient amount of an acid having a  $pK_a$  of 6 or less, preferably 5 or less,

most preferably 4 or less, or an acid-forming material capable of forming an acid having  $pK_a$  characteristics as defined above. The amount of acid or acid-forming material being added is

5 sufficient to protonate more than 0% and up to 22%, preferably 2 to 13%, of the alkaline material. The order of addition is not critical. For example, the alkaline material can be added to the water before, after or simultaneously with the acid or

10 acid-forming material.

This invention applies to a select class of alkaline materials suitable for forming an aqueous absorbent, which do not evolve an acidic gas, e.g.,  $CO_2$  or  $SO_2$ , upon acidification, and which

15 provide enhanced acid gas removal when combined with the appropriate amount of acid or acid-forming material. For example, the invention is advantageously used in conjunction with alkaline solutions suitable for absorbing  $H_2S$  gas and made

20 from alkaline materials such as secondary or tertiary diethanolamines including methyldiethanolamine, diethanolamine, or mixtures thereof. Alkali metal carbonates are not suitable for forming an aqueous absorbent because the

25 carbonates are converted to  $CO_2$  which leaves the system in the off gas and forms the alkali metal salt of the acid added pursuant to this invention. Thus, the acid content of the absorbent solution is not effectively increased. For example, when

30 phosphoric acid is used pursuant to this invention the alkali metal carbonate is converted alkali metal phosphate, e.g.,  $K_3PO_4$ , and  $CO_2$  gas which

leaves the system. Thus, the addition of more and more phosphoric acid fails to effectively increase the acid content until all of the carbonate has been converted to the phosphate and  $\text{CO}_2$ .

5           Only alkaline materials providing enhanced acid gas removal, when combined with an appropriate amount and type of acid or acid-forming material, are suitable in the present invention. The select  
10       class of alkaline materials providing such enhanced acid gas removal are readily determinable using well established procedures in the art by comparing the acid gas removal performance of two aqueous alkaline  
15       absorbent solutions, with and without the requisite protonation of the alkaline material. The alkaline absorbent solution which provides significant, i.e. measurable beyond experimental error, increases in acid gas removal when appropriately protonated, contains the select alkaline absorbent. The  
20       enhanced level of acid gas removal provides treated gaseous mixtures containing very low amounts of acid gas, typically 10 ppm or less, and preferably 1 ppm or less.

25           Suitable alkaline absorbing solutions are selected from water soluble alkaline amines such as an alkanol amine, e.g. monoethanolamine and diethanolamine; alkylalkanolamines such as  
30       methyldiethanolamine, ethylamino-ethanol, cyclohexylaminoethanol, 2-amino-2-methyl-1-propanol and the like. Particularly preferred alkaline materials which have been found to provide enhanced acid gas recovery are secondary or tertiary diethanolamines, such as diethanolamine (DEA),

methyldiethanolamine (MDEA), and mixtures thereof.

The tertiary amines are preferred inasmuch as scrubbing solutions containing tertiary amines selectively absorb hydrogen sulfide over carbon

5 dioxide. The primary and secondary amines provide little, if any, selectivity in absorbing the  $H_2S$  over  $CO_2$ . Mixtures of alkaline materials can also be used. In those instances where the selective absorption phenomena is not important, any aqueous

10 alkaline solution providing enhanced acid gas removal, preferably an aqueous alkaline amine solution, is useful as a scrubbing solution. The concentration of alkaline material in the scrubbing solution can be varied over a wide range from about

15 5 to about 70 wt. % of the alkaline material based on the weight of the scrubbing solution.

Preferably, the scrubbing solution contains 20 to 60 wt. % of the alkaline materials.

Suitable acids that can be used in the

20 present invention can be characterized as strong acids which include any organic or inorganic acid having a  $pK_a$  of 6 or less, preferably 5 or less and most preferably 4 or less. Acids that can be used include phosphoric acid which is preferred

25 because of its low corrosive effects, phosphorous acid, hydrochloric acid, sulfuric acid, sulfurous acid, nitrous acid, pyrophosphoric acid, telurous acid and the like. Also, included as suitable acids

are organic acids such as acetic acid, formic acid,

30 adipic acid, benzoic acid, n-butyric acid, chloroacetic acid, citric acid, glutaric acid, lactic acid, malonic acid, oxalic acid, o-phthalic



acid, succinic acid, o-toluic acid and the like. In addition, acid-forming materials that are capable of forming acids upon contact with water can be used. The acids formed from such acid-forming materials  
5 useful in this invention have a  $pK_a$  of 6 or less, preferably 5 or less and most preferably 4 or less. A suitable acid forming material is sulfur dioxide.

The absolute amount of acid or acid-forming material can also vary over a wide range which is  
10 best expressed in terms of the weight percent of protonation of the alkaline absorbent. The amount of acid used in the invention relative to the amount of alkaline absorbent is narrowly critical and will vary depending upon the type of alkaline absorbent.  
15 For MDEA it has been found that protonation of more than 0% of the alkaline absorbent up to as much as 22% protonation of the alkaline absorbent, preferably not more than 20% protonation, is sufficient. Preferably the range extends from  
20 amounts sufficient to protonate 0.1 to 22% of the alkaline absorbent, preferably to protonate not more than 20% of the alkaline absorbent. More preferably the range encompasses those amounts sufficient to protonate 2 to 13% of the alkaline absorbent. In  
25 the case of the most preferable acid, namely, phosphoric acid, the preferred amount in a 50:50 MDEA:water solution is from more than 0 wt. % up to about 4.5 wt. %, preferably 0.5 to about 2.5 wt. % based on the total weight of the aqueous alkaline  
30 absorbent solution containing the phosphoric acid.

The alkaline absorbing solutions may contain optional adjuvants well known to those

skilled in the art, such as corrosion inhibitors and physical solvents, in addition to water, the alkaline absorbent, and acid or acid-forming material. If foaming becomes a problem, an  
5 antifoaming agent can be added to the absorbent solution at any stage of the process as is well known to those of ordinary skill in the art.

The contacting of the novel aqueous  
10 alkaline scrubbing liquid and the acid gas may take place in any suitable contacting tower. The acid gas to be contacted and removed is hydrogen sulfide which may be present in trace amounts in the gaseous mixture. The contacting between the acid gas and  
15 the aqueous alkaline absorbent scrubbing liquid can be concurrent or countercurrent; counter current being preferred. The contacting takes place in a single phase without regions of phase immiscibility. Temperatures during the contacting  
20 may vary between 40°F. and 250°F., preferably 50°F. to 200°F. Pressures may vary widely. Acceptable pressures are in the range from 0 to 2000 psia, preferably 10 to 1500 psia. As an illustration, the countercurrent contacting to remove the acid gas can  
25 take place over a period of 0.01 second or higher, e.g. up to 10 minutes or more. Contacting may take place when the acid gas containing gas is either in the liquid or gaseous state, although the gaseous state is much preferred.

30 The contacting zone can be a packed tower, plate tower or any known gas scrubber. A stainless steel contacting tower is particularly effective. The tower can be equipped with bubble trays,

preforated trays, Raschig rings or any other known packing material which facilitates contacting between the gas and liquid. After a period of time the absorbent liquid becomes substantially saturated with the acid gas  $H_2S$ . The aqueous alkaline absorbing solution which is substantially saturated with acid gases such as  $H_2S$  must then be regenerated to place it into condition for reuse. Illustratively, the aqueous alkaline absorbent liquid can be about 5 to 95% saturated, preferably about 10 to 90% saturated, when it is regenerated.

The regeneration which can take place in a single liquid phase, is usually accompanied by flashing and passing steam through the liquid until the acid gases are stripped out. Upon entering the regeneration unit the absorbent liquid is substantially saturated as indicated above and in one phase. Stripping of the acid gas may be accompanied using known means by blowing with steam or inert gas according to known techniques. The absorbent liquid is tripped down to a very small amount, illustratively, 0.00004 to 0.02, preferably 0.0003 to 0.01, mol of  $H_2S$  per mol of alkaline material, e.g. MDEA in the absorbent liquid. The absorbing liquid after being regenerated can be recycled back to the contacting tower. Makeup absorbent liquid may be added as needed. Alternatively the saturated absorbent liquid can be regenerated by inert gas, e.g. nitrogen stripping. Air is an example of an inert gas when the alkaline material in the absorbent liquid is inorganic.

As an illustration, in desorption, i.e. regeneration of the absorbent liquid, the acid gas

H<sub>2</sub>S-rich solution from the absorber in which the acid gas containing mixture is contacted with the aqueous alkaline absorbent liquid, can be sent, in the case of high pressure absorption, first to a flash chamber wherein steam, and H<sub>2</sub>S, CO<sub>2</sub>, physically dissolved gases and entrained gases, are flased from the solution at lower pressure. The solution from the flash drum, or from the absorber, in the case of low pressure absorption, can then be steamed stripped in a packed or plate tower. Stripping steam can be generated in or at the base of the stripper. Illustratively, pressure in the flash drum and stripper can be from 1 to 100 psig for the stripper. Illustratively, the temperature of the flash drum can vary from 40°F. to 250°F., preferably 60°F. to 200°F., and in the steam stripper can range between 180°F. to 350°F., preferably 190°F. to 260°F. depending, of course, on stripper pressure. Normally, the gas withdrawn from the top of the stripper contains a high percentage of H<sub>2</sub>S, e.g., 25% or more, and in such cases the gas withdrawn from the top of the stripper can be used in sulfur recovery units, e.g., Claus units, where the H<sub>2</sub>S content is converted into elemental sulfur by known techniques or it can be used as a source of sulfur dioxide in the production of sulfuric acid also according to well known procedures. In those cases where the H<sub>2</sub>S content in the stripper off-gas is lower, e.g., 25% or less, the stripper off-gas can be sent to modified Claus units which are equipped to convert relatively low concentrations of H<sub>2</sub>S into elemental sulfur.

Alternatively, the stripper off-gases of relatively low  $H_2S$  concentrations can be incinerated, whereby the volume of gas subjected to incineration is much lower than the volume of the original gas before treatment according to this invention.

By means of the present invention hydrogen sulfide can now be removed, under normal temperature conditions, from high pressure, e.g., more than 100 psia, gaseous mixtures containing same to very low values such as 1 ppm or less thereby eliminating a very serious safety hazard in the case of natural gas intended for residential use. By means of the present invention,  $H_2S$  can now be removed, under normal temperature conditions, from low pressure, e.g., from 10 up to 30 psia, gaseous mixtures containing same to very low values each 10 ppm or less to comply with Federal EPA regulations.

#### EXAMPLES

The following Examples are presented. The following designations used in the Examples and elsewhere herein have the following meanings.

DEA:	diethanolamine
DIPA:	diisopropanolamine
MDEA:	methyldiethanolamine
25 TEA:	triethanolamine
%:	weight percent unless otherwise specified
liter/min:	liters per minute
ppm:	parts per million on a volume basis
30	which is equivalent to parts per million on a mol basis
°F:	degrees Fahrenheit

- mmscf/d: million standard cubic feet per day  
gpm: gallons per minute  
psia: pounds per square inch pressure  
absolute  
5 psig: pounds per square inch pressure gauge

EXAMPLES 1-3, A and B

- These Examples illustrate the effect of phosphoric acid,  $H_3PO_4$ , on  $H_2S$  removal from an acid gas. In each Example, one liter of an MDEA solution contains:
- |        |        |
|--------|--------|
| $H_2S$ | 0.5%   |
| $CO_2$ | 1.0%   |
| MDEA   | 49.25% |
| $H_2O$ | 49.25% |
- 15 In Example A no phosphoric acid was added to this solution but in Examples 1, 2, 3 and B, 0.1, 1, 2 and 5% respectively, of phosphoric acid,  $H_3PO_4$  was added to the solution, said percentages being based on the total weight of each of said
- 20 solutions. The resulting mixture was refluxed for 335 minutes in a 2-liter flask using an electric heating mantle jacket at a Variac setting of 80 volts and a condenser jacketed with cold tap water. At the end of 335 minutes, the power was turned off
- 25 and the solution was allowed to cool to room temperature. The solution then was pumped at a rate of 9 cc/min. by using a constant displacement piston pump to the top of a vacuum-jacketed, glass column having a one inch inside diameter and 30 sieve
- 30 trays. Line heaters warmed the solution to  $110^\circ F$  before it entered the column.

A feed gas containing 1.5% (15000 ppm)  $H_2S$ , 30%  $CO_2$  and 68.5% nitrogen was heated to 110°F and bubbled through water in a packed vessel to saturate the gas with water. Then the feed gas was passed to a knockout flash to remove any entrained water and thereafter was introduced at the rate of one liter/min. to the bottom of the above-described, trayed column which is maintained at a temperature of 110°F. In the column the feed gas was counter-currently contacted with the MDEA solution. The off gas leaving the top of the absorber was measured in each Example for  $H_2S$  content and the results are given in Table I below:

TABLE I

Ex.	% $H_3PO_4$ *	Mols $H_3PO_4$ Per Mol MDEA	% Proton- ation	PPM $H_2S$ In Off Gas
A	0	0	0	52
1	0.1	0.0024	0.49	12.5
2	1	0.0245	4.9	1
3	2	0.04956	9.9	2
B	5	0.1278	25.6	100

\*Based on the weight of the solution

These results suggest that there is a minimum amount of acid to be added in order to enhance the absorption of the  $H_2S$  gas. These results also show that there is a maximum amount above which  $H_2S$  removal is not enhanced.

A comparison of Examples A and B clearly illustrates that at the rate of 0.1278 mols of phosphoric acid per mol of MDEA the  $H_2S$  content in the off gas is actually increased over and above the amount removed when no acid at all is used.

EXAMPLES 4-7 and C

In each of these Examples an MDEA solution identical to that described in Example A above, that is, with no phosphoric acid addition, was prepared and fed to the top of the absorber at the rate of 7.15 cc/min. The feed gas rate in each case was 0.5 liter/min. Also, the absorber contained only ten sieve trays rather than 30. In Example C no acid was added to the MDEA solution whereas in Examples 4-7 there was respectively added 0.0321%  $H_3PO_4$ , 0.1%  $SO_2$ , 0.14% formic acid and 0.112% HCl based on the weight of the MDEA solution. Thereafter, these Examples were carried out in the same manner as described for Examples 1-3, B and C. The amounts of  $H_2S$  in the absorber off gas is presented in Table II below.

TABLE II

	<u>Exh.</u>	<u>Acid Added</u>	<u>% Acid Added</u>	<u>Mols Acid Per Mol MDEA</u>	<u>% Proton-ation</u>	<u>PPM <math>H_2S</math> In Off Gas</u>
20	C	None	0	0	0	40
	4	$H_3PO_4$	0.0321	0.00079	0.158	1
	5	$SO_2$	0.1	0.00372	0.744	0.75
	6	Formic Acid	0.14	0.00725	1.45	4
25	7	HCl	0.112	0.00731	1.46	2

These Examples show that even very small amounts of acid are effective in dramatically removing  $H_2S$  and reducing  $H_2S$  content in the absorber off gas down to 1 ppm or less. These Examples also illustrate the effectiveness of a wide range of acidic materials including an organic acid, another inorganic acid and an acid-forming material.



EXAMPLES 8 AND D

The effect of adding phosphoric acid to aqueous MDEA on  $H_2S$  absorption was demonstrated in a commercial plant as described below. A 13 tray absorber was operated at 112°F. and 2.3 psig. The feed gas contained approximately 1%  $H_2S$ , 20%  $CO_2$ , 6%  $H_2O$  and 72% nitrogen and was introduced at the bottom of the absorber at a rate of 1.5 mmscf/d. The lean absorbing solution introduced at the top of the absorber contained 43% MDEA and 57% water. In Example D no acid was added to the absorbing solution. In Example 8, 1.61 wt.%  $H_3PO_4$  was added to the absorbing solution thus forming a solution containing 1.61%  $H_3PO_4$ , 42.31% MDEA and 56.08% water. The degree of protonation, the lean solution circulation and the ppm  $H_2S$  in the absorber off gas are given in Table III for Example D and 8.

TABLE III

Ex. No.	% $H_3PO_4$ Added	% Proton-ation of MDEA	Lean Solution Circulation Rate	PPM $H_2S$ In Off Gas
D	0	0	46.4 gpm	110
8	1.61	9.09	52.8 gpm	7

These examples demonstrate that, by adding phosphoric acid, the  $H_2S$  level was reduced by a factor of 15.7 to 1.

EXAMPLES 9 and E

In each of these Examples an MDEA solution identical to that described in Example A above, that

is, with no phosphoric acid addition, was prepared and fed to an absorber at the rate of 13 cc/min. The feed gas rate in each case was 0.5 liter/min. Also, the absorber contained 20 sieve trays. In Example E no acid was added to the MDEA absorbing solution whereas in Example 9 0.0321%  $H_3PO_4$  was added before refluxing. Thereafter these Examples were carried out in the same manner as described for Examples 1-3, B and C. The amounts of  $H_2S$  in the absorber off gas in each case is presented in Table IV below. These Examples show the improvements in using  $H_3PO_4$  in very small amounts in the absorbing solution. The results of these two Examples do not appear to be directly comparable with the results of other Examples because of differences in processing and analytical techniques. However, a noticeable reduction in ppm of  $H_2S$  is demonstrated upon the addition of very small amounts of  $H_3PO_4$  to the absorbing solution.

TABLE IV

Ex.	% $H_3PO_4$	Mols $H_3PO_4$ Per Mol MDEA	% Proton- ation	PPM $H_2S$ In Off Gas
9	0.321	0.0007915	0.158	12.5
E	0	0	0	16

EXAMPLES 10-13 and F

In each of these Examples a MDEA solution identical to that described in Example A above, that is, with no phosphoric acid addition, was prepared and fed to the top of the absorber at the rate of 6.3 cc/min. The feed gas rate in each case was 0.5 liter/min. The absorber contained 20 sieve trays.

In Example F no acid was added to the MDEA solution whereas in Examples 10-13 there was respectively added 0.015%, 0.0321%, 0.07% and 0.25% of phosphoric acid based on the total weight of the MDEA solution. The phosphoric acid was added in each case prior to the refluxing step. Thereafter, these Examples were carried out in the same manner as described for Examples 1-3, B and C. The amounts of H<sub>2</sub>S in the absorber off gas is presented in Table V below.

TABLE V

Ex.	%H <sub>3</sub> PO <sub>4</sub>	Mols H <sub>3</sub> PO <sub>4</sub> Per Mol MDEA	% Proton- ation	PPM H <sub>2</sub> S In Off Gas
F	0	0	0	30
10	0.015	0.00037	0.074	28
11	0.0321	0.00079	0.158	2
12	0.07	0.00173	0.345	7
13	0.25	0.00618	1.24	2

These Examples show that even very small amounts of acid are effective in removing H<sub>2</sub>S and reducing H<sub>2</sub>S content in the absorber off gas down to low ppm levels. The results of these Examples are not directly comparable with the results of other Examples described herein because of certain differences in processing and analytical techniques.

EXAMPLES 14-18 and G-Q

These Examples demonstrate various alkaline materials which have been found useful in the present invention, as compared to alkaline materials which do not fall within the select class of materials which provide for increases in acid gas scrubbing, i.e., removal, when compared to the

corresponding absorbent solution free of acid or acid-forming materials. Alkaline absorbent solutions containing various alkaline material were prepared and tested using those procedures set forth for Examples 1-3, A and B, except for variations in alkaline solution pump rate as set forth in the footnotes for Table VI. Examples G-J correspond to the use of triethanolamine (TEA). Examples K-M correspond to the use of diisopropanolamine (DIPA). Examples 14 and N-P correspond to the use of diethanolamine (DEA). Examples 15-18 and Q correspond to the use of a DEA/MDEA mixture. Varying amounts of  $H_3PO_4$  were added to each solution, given in weight percent, moles of acid per mole alkaline material, and % protonation as set forth in Table VI. The PPM  $H_2S$  in the absorber off gas for each solution is given in Table VI.

---

TABLE VI

5	Ex.	Alkaline % Solution	H <sub>3</sub> PO <sub>4</sub>	Mols H <sub>3</sub> PO <sub>4</sub> Per Mol		PPM H <sub>2</sub> S In Off Gas
				Alkaline %	Proton- Material ation	
10	G	TEA <sup>a</sup>	0	0	0	170
	H	TEA <sup>a</sup>	0.5	0.0152	3.04	690
	I	TEA <sup>a</sup>	1.0	0.0304	6.08	1,900
	J	TEA <sup>a</sup>	1.75	0.0532	10.6	3,000
15	K	DIPA <sup>b</sup>	0	0	0	57
	L	DIPA <sup>b</sup>	0.3	0.0101	2.04	700
	M	DIPA <sup>b</sup>	0.6	0.0204	4.07	1,100
	N	DEA <sup>c</sup>	0	0	0	5
20	14	DEA <sup>c</sup>	0.3	0.0129	2.57	0
	O	DEA <sup>c</sup>	0.6	0.0257	5.14	8
	P	DEA <sup>c</sup>	1.5	0.0643	12.9	200
	Q	DEA/MDEA <sup>d</sup>	0	0	0	60
25	15	DEA/MDEA <sup>d</sup>	0.35	0.00839	1.68	2
	16	DEA/MDEA <sup>d</sup>	0.7	0.0168	3.36	<0.5
	17	DEA/MDEA <sup>d</sup>	1.4	0.0336	6.71	<0.5
	18	DEA/MDEA <sup>d</sup>	2.5	0.0559	12.0	<0.5

<sup>a</sup>50% TEA/50% H<sub>2</sub>O at 12.3 ml/min.

<sup>b</sup>40% DIPA/60% H<sub>2</sub>O at 10.3 ml/min.

<sup>c</sup>25% DEA/75% H<sub>2</sub>O at 13.2 ml/min.

<sup>d</sup>5% DEA/45% MDEA/50% H<sub>2</sub>O at 13 ml/min.

The results of these Examples demonstrate that only a select class of alkaline materials are useable in aqueous alkaline solutions providing increased acid gas removal. These Examples also  
5 demonstrate that the critical amount of % protonation will vary between different alkaline absorbents, with effective DEA % protonation narrower and effective DEA/MDEA % protonation broader relative to the range for MDEA.

CLAIMS:

1. Composition for mixing with water to provide an aqueous, alkaline liquid which does not evolve an acidic gas upon acidification, for scrubbing hydrogen sulfide-containing acid gases comprising (1) an alkaline material capable of absorbing  $H_2S$  in aqueous solution and (2) an acid having a  $pK_a$  of 6 or less or an acid-forming material capable of forming in aqueous medium an acid having a  $pK_a$  of 6 or less in an amount sufficient to protonate greater than 0% and not more than 22% of said alkaline material; such that said alkaline liquid provides for increased hydrogen sulfide removal when compared to the corresponding alkaline liquid free of said acid or acid-forming material.
2. Composition as claimed in claim 1 wherein said acid or acid forming material is present in an amount sufficient to protonate 2 to 13% of said alkaline material.
3. Composition as claimed in any of the preceding claims 1-2 wherein said acid has a  $pK_a$  of less than 4.
4. Composition as claimed in any of the preceding claims 1-3 wherein said alkaline material is a secondary or tertiary diethanolamine, e.g. methyldiethanolamine, or mixture thereof.
5. Composition as claimed in any of the preceding claims 1-4 wherein an acid is used and said acid is phosphoric acid, formic acid or hydrochloric acid.

6. Composition as claimed in any of the preceding claims 1-4 wherein an acid-forming material is used and said acid-forming material is sulphur dioxide.

5 7. In a process for removing hydrogen sulfide as a constituent from gases by washing the gases with an aqueous alkaline scrubbing liquid containing an alkaline material which does not form an acidic gas upon acidification, and subsequently regenerating the scrubbing liquid, the improvement which comprises using in said scrubbing liquid, (1)  
10 an acid having a  $pK_a$  of 6 or less or an acid-forming material capable of forming an acid having a  $pK_a$  of 6 or less in aqueous medium in an amount sufficient to protonate more than 0% but not more than 22% of said alkaline material, and (2) an  
15 alkaline material which provides for increased hydrogen sulfide removal when compared to the corresponding alkaline liquid free of said acid or acid-forming material.

20 8. Improvement as claimed in claim 7 wherein said alkaline material is a secondary or tertiary diethanolamine, e.g. methyldiethanolamine, or mixtures thereof.

25 9. Improvement as claimed in any of the preceding claims 7-8 wherein an acid is used and said acid is phosphoric acid, formic acid or hydrochloric acid.

10. Improvement as claimed in any of the preceding claims 7-8 wherein an acid-forming material is used and said acid-forming material is sulphur dioxide.



11. An aqueous alkaline solution for scrubbing hydrogen sulfide-containing acid gases which comprise 5 to 60 wt. % of an alkaline material, which does not form an acidic gas upon acidification, based on the weight of the scrubbing liquid, an acid having a  $pK_a$  of 6 or less or an acid-forming material capable of forming in aqueous medium an acid having a  $pK_a$  of 6 or less, said acid or acid-forming material being present in an amount sufficient to protonate more than 0 % but not more than 22 %, e.g. 0.1 % to 22 %, of said alkaline material; such that said alkaline liquid provides for increased hydrogen sulfide removal when compared to the corresponding alkaline liquid free of said acid or acid-forming material, with the balance of said solution being water.

12. Solution as claimed in claim 11 wherein said acid has a  $pK_a$  of less than 4.

13. Solution as claimed in any of the preceding claims 11-12 wherein said acid or acid-forming material is present in an amount sufficient to protonate from about 2 to about 13 % of said alkaline material in said solution.

14. Solution as claimed in any of the preceding claims 11-13 wherein an acid is used and said acid is phosphoric acid, formic acid or hydrochloric acid.

15. Solution as claimed in any of the preceding claims 11-13 wherein an acid-forming material is used and said acid-forming material is sulphur dioxide.

16. Solution as claimed in any of the preceding claims 11-15 wherein said alkaline material is a secondary or tertiary diethanolamine, e.g. methyldiethanolamine, or mixture thereof.

5           17. An aqueous alkaline solution for scrubbing hydrogen sulfide-containing acid gases which comprise 5 to 60 wt. % of a secondary or tertiary diethanolamine or mixtures thereof, based on the weight of the scrubbing liquid, an acid having a  $pK_a$  of 6 or less or an acid-forming  
10 material capable of forming in aqueous medium an acid having a  $pK_a$  of 6 or less, said acid or acid-forming material being present in an amount sufficient to protonate more than 0% but not more  
15 than 22% of said secondary or tertiary diethanolamine or mixtures thereof.

          18. In a process for removing hydrogen sulfide as a constituent from gases by washing the  
20 gases with an aqueous alkaline scrubbing liquid containing a secondary or tertiary diethanolamine or mixtures thereof, and subsequently regenerating the scrubbing liquid, the improvement which comprises using in said scrubbing liquid an acid having a  
25  $pK_a$  of 6 or less or an acid-forming material capable of forming an acid having a  $pK_a$  of 6 or less in aqueous medium in an amount sufficient to protonate more than 0% but not more than 22% of said secondary or tertiary diethanolamine or mixtures thereof.